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Using Active Surface Plasmons in a Multibit Optical Storage Device to Emulate Long-Term Synaptic Plasticity

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Artificial intelligence takes inspiration from the functionalities and structure of the brain to solve complex tasks and allow learning. Yet, hardware realization that simulates the synaptic activities realized with electrical devices still lags behind computer software implementation, which has improved significantly during the past decade. Herein, the capability to emulate synaptic functionalities by exploiting surface plasmon polaritons (SPPs) is shown. By depositing photochromic switching molecules (diarylethene) on a thin film of gold, it is possible to reliably control the electronic configuration of the molecules upon illumination cycles with UV and visible light. These reversible changes modulate the dielectric function of the photochromic film and thus enable the effective control of the SPP dispersion relation at the molecule/gold interface. The plasmonic device displays fundamental functions of a synapse such as potentiation, depression, and long-term plasticity. The integration of such plasmonic devices in an artificial neural network is deployed in plasmonic neuroinspired circuits for optical computing and data transmission.

1. Introduction

In the nervous system, the synapse is the fundamental element responsible for signal transduction and hence enables communication between neurons. The transduction occurs in the synapse through chemical processes that regulate the synaptic signal strength via an increase or a decrease of the signal intensity. This occurs by the controlled release of neurotransmitters from the axons of one neuron which bind to the receptors on the dendrites of a second neuron. This dynamic ability of the synapses to modulate the exchange of chemical information between neurons is considered the basis of learning processes and memory.

Inspired by these processes—and following the path already envisioned by software engineering—neuromorphic device engineering aims to realize artificial neurobiological hardware using physical elements to mimic the interconnected nodes which can be organized in so-called artificial neural networks (ANNs). The implementation of this operating concept in hardware ANNs requires the identification of a physical device that can reliably serve as a node. This element must therefore be capable to simultaneously conduct signal processing (continuous function with the input as the variable) and information storage (rewriteable synaptic weights). The interconnection of physical synapses organized in ANNs ultimately allows to shift machine learning capabilities from software to hardware, thereby boosting computing performance and reducing power consumption.

As introduced earlier, the state of a physical property in a neuromorphic device changes during the "learning" process through an external stimulus, leading to an increase of the synaptic weight (potentiation). Vice versa, the synaptic state can be reversibly decreased with a second stimulus (depression).[1] These processes are schematically shown in **Figure 1**a, whereby pulsed external stimuli lead to potentiation and depression, respectively, of the synaptic weight. The continuous change of the synaptic weight (which allows multistate storage) has so far

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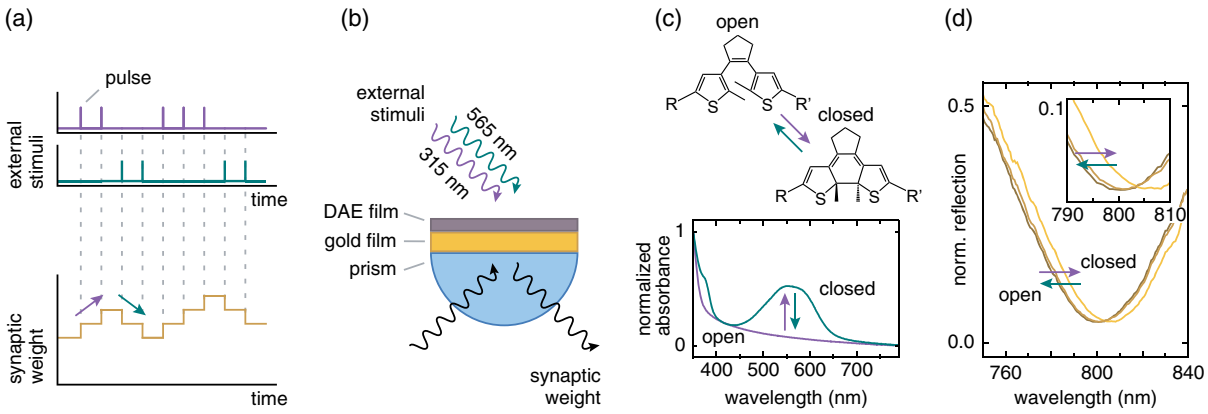

Figure 1. a) Schematic depiction of the time evolution process related to potentiation and depression of the synaptic weight upon external optical stimulation using two pulsed light sources (wavelengths 315 and 565 nm). b) Schematic representation of the artificial plasmonic synapse based on Kretschmann configuration. c) The pulsed light (315 and 565 nm) causes ring closure and ring opening, respectively, of the DAE molecule (for R = 4-acetylthiophenyl and R' = 3,5-di-*tert*-butylphenyl[5]) and is displayed in the UV–vis absorption spectra. d) The SPP absorption dip in the attenuated total reflection spectra shifts reversibly backward and forward depending on the isomerization state of the DAE molecules, as also shown in the zoom-in.

been realized using electrical devices such as memristors or field-effect transistors.[2–5] These electrically driven devices, fabricated with organic and inorganic materials, utilize voltage to regulate the input value and detect the current as the output. Thus, an electrical information cascade with several device elements in series can be realized by biasing and processing each of them individually along the signal propagation and not by applying a voltage at the beginning and the end of the entire device series.

Although the optical approach exhibits many advantages for signal transduction, optically driven synaptic emulations have barely been reported so far.[6,7] The interest is however slowly increasing and has led, for instance, to the fabrication of photonic memristors for neuromorphic computing.[8] In optical devices the input has the same physical value (e.g., phase, intensity) as the output and thus a signal cascade can be achieved *without* repetitive biasing and processing. Only Abbe's law of diffraction hinders the embedding of such systems into subwavelength-scaled devices. To overcome this issue, active plasmonic devices have been developed that surpass the diffraction limit by photon coupling and by allowing the realization of a high integration density.[9–12] They work by coupling surface plasmons to photons, for example, at a metal/dielectric interface, in turn generating a propagating electromagnetic wave, the so-called surface plasmon polariton (SPP).[13] As the SPP is based on a surface phenomenon, both phase and intensity are most sensitively dependent on the interfacial environment and thus critically depend on molecules located at the surface, a property commonly exploited in sensor applications.[14,15] Especially the fact that SPPs can propagate on metal/dielectric interfaces enables the fabrication of photonic network chips on a subwavelength scale. This allows machine learning processes based on optics with photochromic molecules or optical phase change materials.[16]

In this work, we utilize the properties of the SPP to demonstrate learning functionalities with a plasmonic switching device. Using a layer of thermally stable photochromic diarylethene (DAE) molecules deposited on a thin film of gold, we demonstrate reversible and reliable switching of the SPP propagation upon external stimulation with light. The external light pulses control the SPP propagation by switching the configuration of the DAE molecules and thereby emulate the functionality of potentiation and depression of the synaptic weight. Moreover, upon implementation in a plasmonic neuromorphic device, we emulated the so-called long-term plasticity (LTP) of a synapse, which is the biological process for the long retention time of the synaptic weight and the essential functionality involved in the long-term learning process.

2. Experimental and Results

2.1. Device Configuration

The experiments are all conducted at room temperature and use total internal reflection (TIR) in Kretschmann configuration, this being an efficient method for SPP excitation for vertical material stacks.[17,18] The optical excitation of SPPs in the plasmonic synaptic device is shown in Figure 1b (a detailed schematic of the setup is shown in Figure S1, Supporting Information). To achieve the Kretschmann configuration, a thin gold film (35 nm) was evaporated on a glass substrate and positioned on a prism (both glass and prism made of BK-7). On top of the Au film a layer of DAE was spin coated with 25 nm thickness (Figure S2, Supporting Information, for details of the synthesis). The choice of DAE as a photochromic molecule is based on its reliable switching behavior without change of the inner dipole to ensure that just the dielectric environment causes modulation.[19,20] Note that the specific DAE derivative used has been initially designed as a precursor for self-assembled monolayers on gold; however, to increase the dielectric contrast it has been used as a thin film instead.

The molecular layer is initially in the open configuration characterized by the absence of absorption in the visible range of the spectrum (see Figure 1c). Upon illumination with UV light, the colorless open isomer undergoes a photochemically induced ring-closure reaction to the fully conjugated closed isomer. The occurrence of this is valence bond tautomerization that is indicated by the broad absorption peak

centered at 550 nm. By illumination with visible light, the closed isomer undergoes the reverse ring-opening reaction and thereby reversibly switches back to the initial open isomer.[21–23] Light-emitting diodes of 315 and 565 nm wavelength (with irradiance of 10^{-6} μW mm^{-2}) were used for this. The longer the illumination period, the more molecules assume the respective configuration, finally leading to a photostationary state (i.e., the ratio between open and closed isomers remains constant upon further illumination). As a result of the change in optical gap of the DAE between the open and closed form, the dielectric function ε_d of the DAE film is modulated.

2.2. Active Optical Modulation

Using polarized white light shining through the prism in Kretschmann configuration, the reflection spectrum was recorded as a function of the incident angle. At a particular incident angle, the wave vector of light parallel to the Au surface is such that SPP is induced and, as a result, a dip in the reflection spectrum is measured. Figure 1d shows the SPP absorption dip in the attenuated total reflection spectra measured with 42.5° incident angle. The minima for the open isomer is located at 795 nm. Upon illumination with UV (315 nm for 60 s), the molecules switch to the closed isomers and as a consequence the SPP dip shifts to 804 nm. As observed in the UV–vis spectra, the SPP signal displays reversibility, and by illuminating with visible light (565 nm for 150 s), the SPP dip is restored to the original position. By means of the transfer matrix method and utilizing the dielectric function of the open isomer calculated using the Kramers–Kronig relation[24,25] (see also Figure S3, Supporting Information), the resulting dispersion relation of the collection of these reflection dips for each incident energy and wave vector is shown in **Figure 2**. The color displays the normalized reflection; the more SPPs are excited, the more attenuated reflection occurs and, hence, the darker the color on the map. Upon switching from the open to the closed isomer, the change in the optical gap of the DAE leads to a change in the dielectric function ε_d.

By adjusting the incident angle of the polarized excitation light (and thus the incoming wave vector of the light parallel to the gold surface) the SPP frequency can be shifted into and out of the frequency region where the DAE film absorbs, i.e. ON resonance and OFF resonance, respectively. Therefore, two kinds of modulations of the SPP can be envisioned. First, at ON resonance, the SPP couples with the absorption state of the DAE film, which leads to a slight increase of the signal as well as a broadening within the reflection spectrum (with respect to that of the open isomer). This is shown in Figure 2b, where the intensity of the reflected light is greater within the ON resonance regime (490 nm–620 nm), meaning fewer SPPs are excited and the color map is lighter. The broadening of the dip in the reflection spectrum is shown within the dispersion relation as an increase in the distance between the isolines. Generally, upon strong interaction between a dielectric and SPP generated on the gold film, splitting of the reflection spectrum due to the anticrossing effect of the SPP is observed. Thereby the oscillations of the electrons in the closed conjugation couple to the generated SPPs and inhibit an intersection of these two dispersion relation modes.[26,27] However, due to the weak coupling of the SPP with the

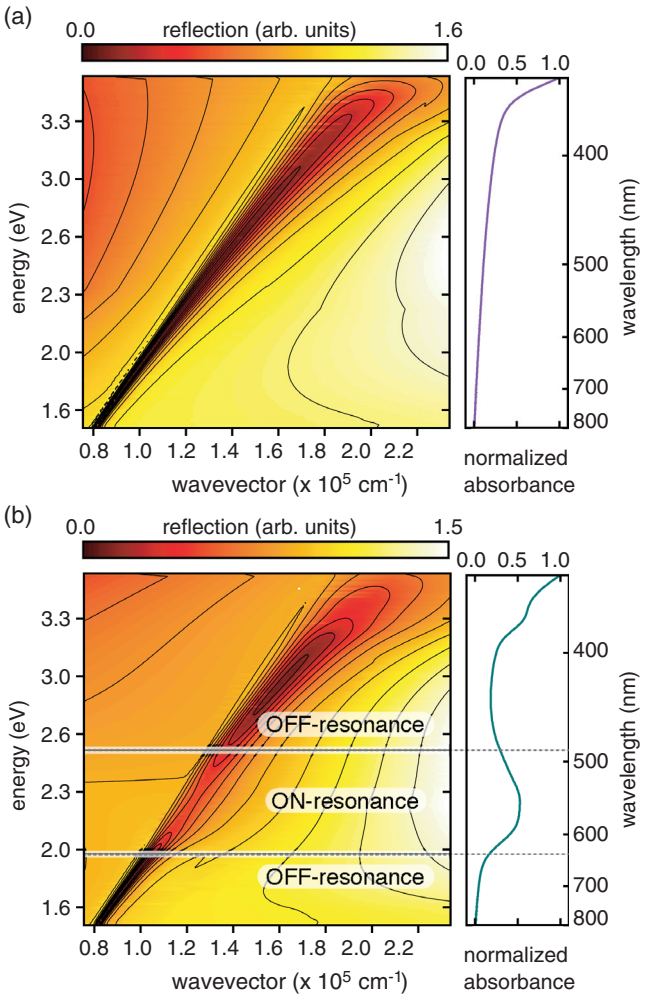

Figure 2. Color map of the dispersion relation of the SPP for the a) open and b) closed isomer respectively. The corresponding UV–vis spectra are displayed on the right. The color map displays the normalized reflection as a function of the energy (wavelength) and wave vector. The higher the reflection within the dispersion relation, the lighter the color on the map.

absorption of the DAE molecule used in our configuration, only a broadening and increase of reflection are seen in the dispersion relation rather than a strict splitting.

Second, at OFF resonance (300–450 nm and 650–800 nm), a redshift of the reflection dip occurs with respect to the open isomer. This shift is particularly clear in the narrowest portion of the dispersion relation around 750 nm. Upon cycling between the two isomers, a fully reversible modulation of the SPP signal is observed, as shown in Figure 1d. Although both the ON resonance and OFF resonance modulate the SPPs fully reversibly, we operated in OFF resonance to prevent any unintended isomerization of the photochromic molecules through the SPPs.

2.3. LTP Emulation

To emulate the LTP, the described OFF resonance regime was used. To obtain the narrowest reflection dip (see Figure S4,

Supporting Information), an incident angle (43°) and wavelength (730 nm) was designated. For this specific combination (and hence at the corresponding wave vector parallel to the gold surface), the sample was irradiated with light pulses acting as external stimuli.

Upon illumination of the DAE film (originally in open configuration) with UV light pulses (1 s), a stepwise increase in the fraction of closed isomers is achieved. This stepwise increase results in a change of the detected reflection intensity and is manifested as a stepwise increase of the relative reflectivity R/R_0, as shown in **Figure 3**a.

Each step can be understood as one of the optical multistates between the minimum (photostationary open state) and the maximum reflectivity (photostationary closed state). As discussed in the introduction (and shown in Figure 1a), this behavior is equivalent to the classical learning process, which follows the potentiation induced by external stimulus (light pulse), leading to an increase of the synaptic weight (relative reflectivity R/R_0).

This synaptic weight can be reversibly decreased with a second stimulus. This is achieved by illumination with visible light pulses (1 s), leading to depression of the relative reflectivity R/R_0. Figure 3b shows the reversible pulsed modulation of the combination of potentiation and depression cycles. To correct for the lower-backward photoconversion efficiency caused by the smaller quantum yield of the closed isomer, the overall intensity of the visible light used for ring opening was higher. In addition, as extended periods of switching of the molecules induce some fatigue of the photochromic molecules (see Figure S5, Supporting Information), we limited the total illumination time to 20 pulses at 315 nm and 30 pulses at 565 nm. The resulting modulation leads to a linear increase in reflection intensity R up to 1.4× the initial reflection intensity R_0. The reflection intensity shows distinct state values corresponding to the number of applied pulses. As each value remains in a stable state upon pulsed illumination, this long retention time resembles the synaptic LTP. Therefore, the overall behavior allows multistate storage in which the writing, erasing, and reading processes occur optically on a subwavelength scale within an artificial plasmonic synapse.

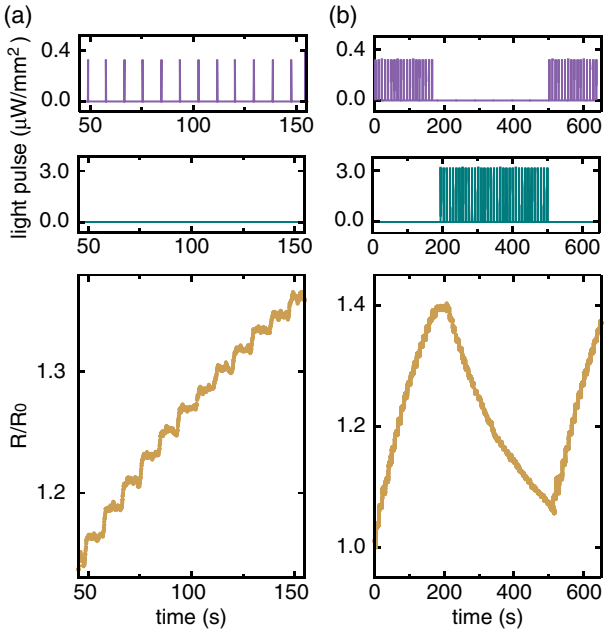

Figure 3. a) The timeline indicates the UV–light pulses (315 nm) which induce the stepwise change in the relative reflectivity R/R_0, emulating potentiation. b) Visible-light pulses (565 nm) lead to the reversible stepwise decrease in R/R_0. The R/R_0 values were measured at 730 nm and 43° incidence angles.

2.4. Retention Characteristics of the Synaptic Weight

To examine the switching reliability and retention of the DAE molecules, a bistate switching between two states was conducted. **Figure 4**a shows the behavior of the artificial plasmonic synapse upon 50 illumination cycles (8 s with 315 nm and 20 s with 565 nm per cycle). The reflectivity measurements were carried out using the same parameters as described earlier (730 nm at 43°). By defining the ON state as the state with the higher relative reflectivity R/R_0 (the upper data points), as opposed to the OFF state (the lower data points), the initial difference $\Delta(R/R_0) = 0.3$ can be sustained over almost 50 cycles. It has to be noted that when increasing the total illumination time (8 and 20 for UV and visible light, respectively), it is possible to switch the DAE molecule between the open and closed isomers enriched photostationary states, leading to a higher $\Delta(R/R_0)$. However, this initial difference decreases exponentially due to fatigue; thereby, the two states can reliably be distinguished only for a limited number of cycles (see Figure S5, Supporting Information).

Due to the stability of each state, the device can be implemented as analogous to nonvolatile optical memory, as the DAE molecules do not require external power to maintain their isomeric state. To evaluate the retention characteristics, we considered that the states of the DAE film show a high retention time and stability toward the reading processes through SPP. To investigate the retention time of this DAE-SPP combination, the sample was first illuminated with UV light (315 nm for 4 min) and the resulting relative reflectivity R/R_0 measured as a function of the (post-illumination) time (see Figure 4b). Likewise, the sample was illuminated with visible light (565 nm for 5 min) and the

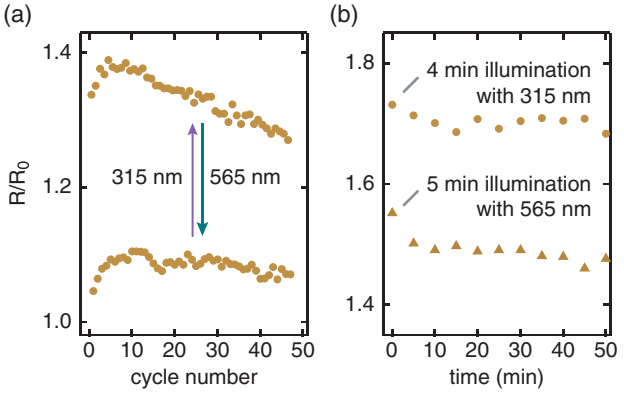

Figure 4. Switching reliability and state retention. a) ON–OFF characteristics of the artificial plasmonic synapse upon cycling (8 s with 315 nm and 20 s with 565 nm per cycle). b) The DAE film was irradiated first with UV light (4 min, circles), then with visible light (5 min, triangles), and the resulting relative reflectivity at a fixed wavelength and angle (730 nm; 43°) plotted over time.

time evolution of R/R_0 was examined. A stable retention for both states is observable in the measured time window, indicating that the DAE-SPP modulation can be generally exploited for nonvolatile neuromorphic operations.

3. Conclusions

In conclusion, we fabricated an optical artificial synapse by exploiting the modulation of SPPs generated on a thin Au film. The SPP modulation is achieved by coating the Au film with the photochromic switching molecule DAE. By measuring the SPP absorption dip in the attenuated total reflection, we demonstrated that the optical switch of the molecular film modulates the relative reflectivity at the DAE/Au interface. By controlling the irradiation time, it is possible to access stable multiple state values. As a result, nonvolatile optical storage behavior was demonstrated. Using two different pulsed light sources as external stimuli, the long-term synaptic behavior can therefore be emulated by interpreting the device's relative reflectivity as synaptic weight. The latter can be stepwise controlled through the induced potentiation and depression action as a result of the external illumination, leading to the DAE conjugation's closing and opening.

Given the nature of this plasmonic synapse, the LTP behavior could exploit both phase and intensity modulation for the implementation of the device in an artificial network. This would allow the development of artificial intelligence through analogous signal transduction capable of incorporating common algorithms, such as backpropagation. Hence, in the near future, optical signal modulation by means of photochromic molecules can become a viable and promising approach to design photonic artificial neuromorphic networks, thereby overcoming the limits associated with the von Neumann architecture.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

artificial intelligence, long-term plasticities, surface plasmon polaritons, switching molecules

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[1] M. A. Zidan, J. P. Strachan, W. D. Lu, *Nat. Electron.* **2018**, *1*, 22.
[2] M. Giulioni, F. Corradi, V. Dante, P. Del Giudice, *Sci. Rep.* **2015**, *5*, 1.
[3] Z. Wang, S. Joshi, S. Savel'ev, W. Song, R. Midya, Y. Li, M. Rao, P. Yan, S. Asapu, Y. Zhuo, H. Jiang, P. Lin, C. Li, J. H. Yoon, N. K. Upadhyay, J. Zhang, M. Hu, J. P. Strachan, M. Barnell, Q. Wu, H. Wu, R. S. Williams, Q. Xia, J. J. Yang, *Nat. Electron.* **2018**, *1*, 137.
[4] Y. van de Burgt, A. Melianas, S. T. Keene, G. Malliaras, A. Salleo, *Nat. Electron.* **2018**, *1*, 386.
[5] E. J. Fuller, S. T. Keene, A. Melianas, Z. Wang, S. Agarwal, Y. Li, Y. Tuchman, C. D. James, M. J. Marinella, J. J. Yang, A. Salleo, A. A. Talin, *Science* **2019**, *364*, 570.
[6] T. W. Ebbesen, C. Genet, S. I. Bozhevolnyi, *Phys. Today* **2008**, *61*, 44.
[7] S. Seo, S. H. Jo, S. Kim, J. Shim, S. Oh, J. H. Kim, K. Heo, J. W. Choi, C. Choi, S. Oh, D. Kuzum, H. S. P. Wong, J. H. Park, *Nat. Commun.* **2018**, *9*, 1.
[8] E. Goi, Q. Zhang, X. Chen, H. Luan, M. Gu, *PhotoniX* **2020**, *1*, 1.
[9] F. Zhou, Z. Zhou, J. Chen, T. H. Choy, J. Wang, N. Zhang, Z. Lin, S. Yu, J. Kang, H. S. P. Wong, Y. Chai, *Nat. Nanotechnol.* **2019**, *14*, 776.
[10] P. Ambs, *Adv. Opt. Technol.* **2010**, *2010*, 15.
[11] T. J. Davis, D. E. Gómez, A. Roberts, *Nanophotonics* **2016**, *6*, 543.
[12] D. M. Koller, A. Hohenau, H. Ditlbacher, N. Galler, F. Reil, F. R. Aussenegg, A. Leitner, E. J. W. List, J. R. Krenn, *Nat. Photonics* **2008**, *2*, 684.
[13] J. Zhang, L. Zhang, W. Xu, *J. Phys. D: Appl.* **2012**, *45*, 113001.
[14] J. Homola, S. S. Yee, G. Gauglitz, *Sens. Actuators, B Chem.* **1999**, *54*, 3.
[15] B. Prabowo, A. Purwidyantri, K.-C. Liu, *Biosensors* **2018**, *8*, 80.
[16] M. Rudé, R. E. Simpson, R. Quidant, V. Pruneri, J. Renger, *ACS Photonics* **2015**, *2*, 669.
[17] E. Kretschmann, *Z. Phys.* **1971**, *241*, 313.
[18] L. Chen, Z. Cao, F. Ou, H. Li, Q. Shen, H. Qiao, *Opt. Lett.* **2007**, *32*, 1432.
[19] F. Ye, J. M. Merlo, M. J. Burns, M. J. Naughton, *Nanophotonics* **2014**, *3*, 33.
[20] M. Irie, *Proc. Jpn. Acad. Ser. B* **2010**, *86*, 472.
[21] M. Irie, M. Mohri, *J. Org. Chem.* **1988**, *53*, 803.
[22] M. Irie, *Chem. Rev.* **2000**, *100*, 1683.
[23] M. Irie, T. Fukaminato, K. Matsuda, S. Kobatake, *Chem. Rev.* **2014**, *114*, 12174.
[24] M. Born, E. Wolf, *Principles of Optics*, Cambridge University Press, Cambridge **1999**.
[25] S. Hunklinger, *Festkörperphysik*, De Gruyter, Berlin **2014**.
[26] A. J. Moilanen, T. K. Hakala, P. Törmä, *ACS Photonics* **2018**, *5*, 54.
[27] P. Törmä, W. L. Barnes, *Reports Prog. Phys.* **2015**, *78*, 013901.